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(56) Documents cited

EP 0257468 A2 WO 90/03632 A1 US 4945708 A

US 4813541 A US 4519515 A US 4511052 A

US 4505399 A US 4502605 A

(58) Field of search

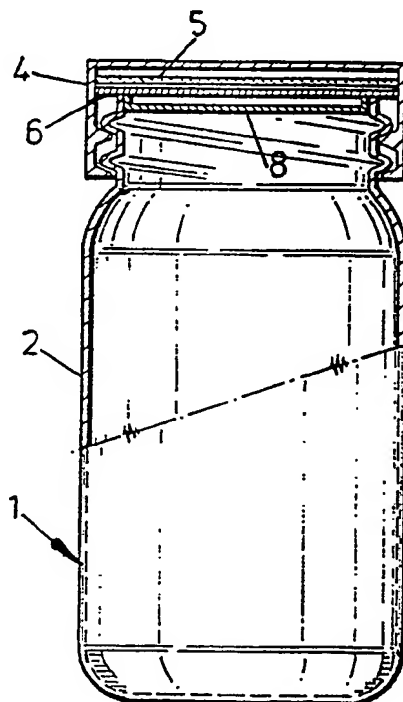
UK CL (Edition K) B8C CWS4 CWS8, B8F FBG, B8T

TTB TTC TTT

INT CL<sup>5</sup> B65D 55/02 55/06, G09F 3/02 3/03

(54) **Packaging with air-sensitive tampering indicator**

(57) Packaging is associated with an air sensitive tampering indicator element 5 which provides an observable change on exposure to air, eg. as a result of removal of a lid 4 from a container 1. The indicator element may be a dye such as crystal violet lactone formulated in a suitable solvent for application to a substrate (eg. thin layer chromatography paper) which incorporates an acidic material which promotes a colour formation reaction. The indicator may be covered by a membrane 6 which is fractured when the lid is opened. In other embodiments the indicator element may have the form of a sealing tape comprising clear film overlying a layer of treated paper. The tape may seal the lid of a jar or may seal a package.



**FIG. 1**

At least one drawing originally filed was informal and the print reproduced here is taken from a later filed formal copy.

This print takes account of replacement documents submitted after the date of filing to enable the application to comply with the formal requirements of the Patents Rules 1990.

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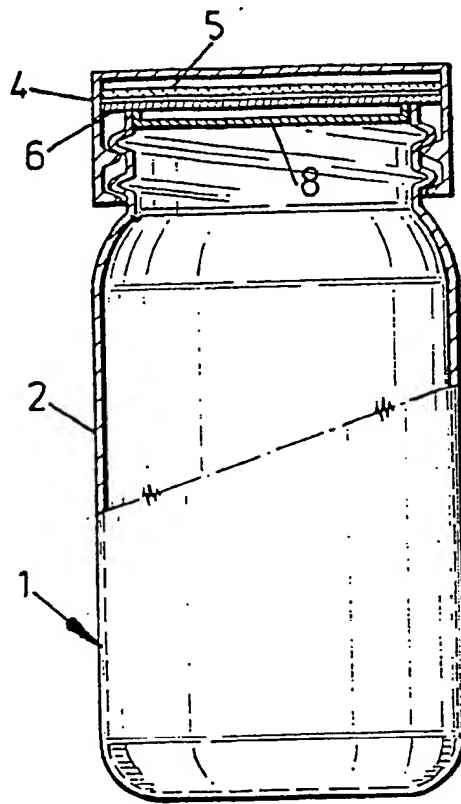


FIG. 1

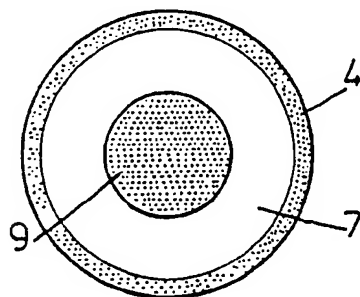


FIG. 3

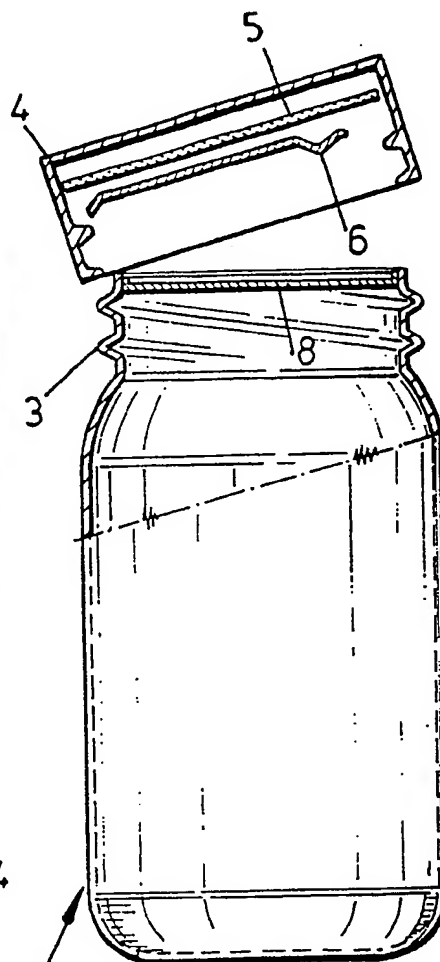


FIG. 2

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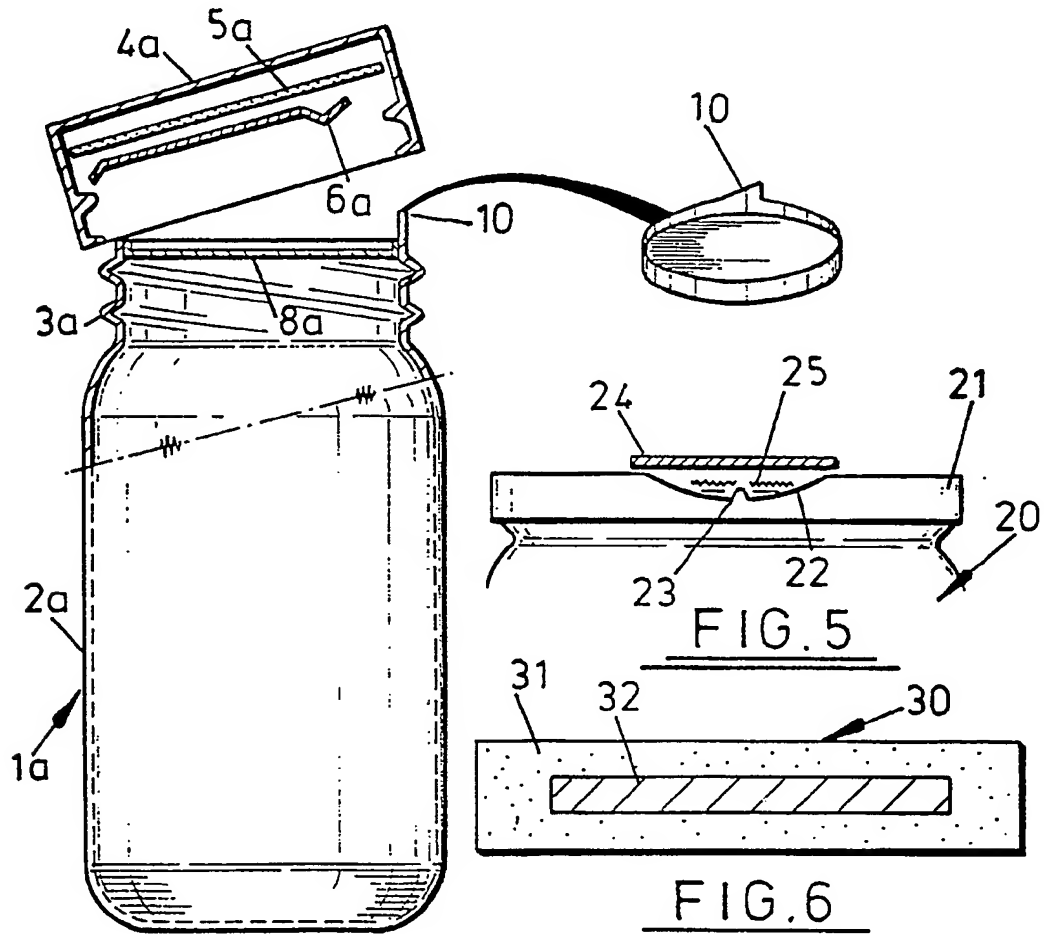


FIG. 4

FIG. 5

FIG. 6

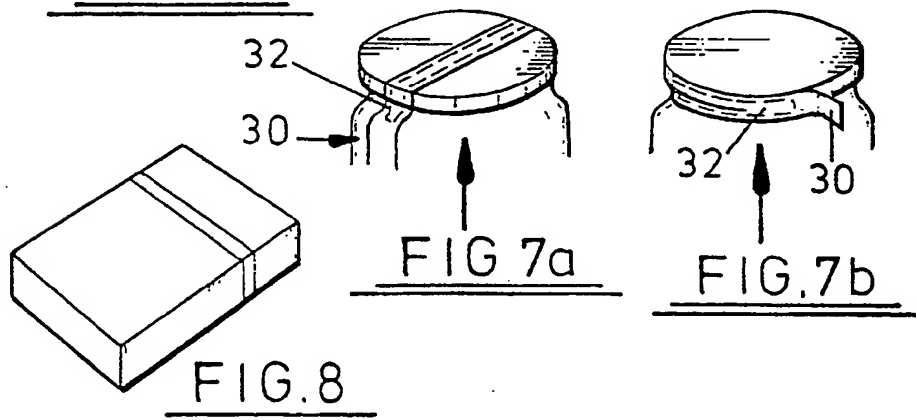


FIG. 7a

FIG. 7b

FIG. 8

### PACKAGING

The present invention relates to packaging.

Many products are sold in packaging (eg. a container such as a bottle, jar etc) which can be opened and then closed again without any visible change to the container. As such there is the problem that prior to the sale of the product it is possible for the package to be opened, the contents to be tampered with, and the package then closed again. The purchaser of the product will be unaware that the contents have been tampered with. This is potentially dangerous in that harmful objects or chemicals may be introduced into the package and cause injury or illness to the end user of the contents of the package. A similar problem exists if the packaging is of a material which may be penetrated by the needle of a syringe, in which case a harmful substance may be injected into the package which would leave minimal or no evidence of tampering.

A further problem in the packaging field is in relation to counterfeit goods. These are goods which have been produced by unauthorised copying of the original articles, and examples include video tapes, audio tapes, pharmaceuticals, and spare parts for motor vehicles. The counterfeit goods will generally be supplied in packaging identical to that of the genuine article, and the purchaser has no immediate way of checking whether or not the goods are counterfeit. At the very least, the supply of counterfeit goods will involve a loss of revenue to the manufacturer of the genuine product and moreover may be potentially dangerous to the purchaser in the case where spare parts for motor vehicles are involved.

According to the present invention there is provided packaging associated with an air sensitive indicator element which is prevented from contact with air, said indicator element being such as to provide an observable change upon exposure to air.

In accordance with the invention therefore the exposure of the indicator element to air produces an observable change, preferably a colour change. The indicator may for example incorporate a pattern or a message which is revealed (by virtue of the colour change) only upon exposure to air.

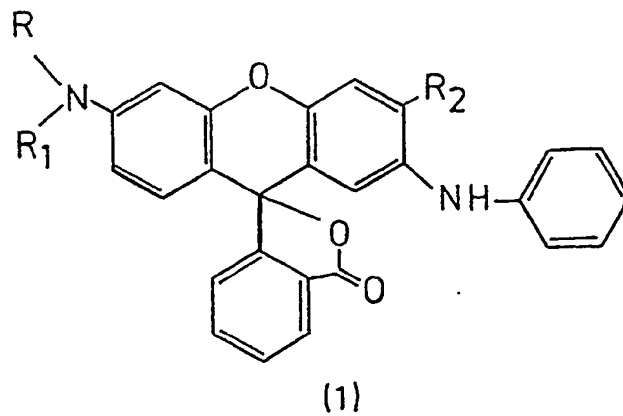
The invention is applicable both to tamper evident packaging as well as packaging intended to provide protection against counterfeiting. In the former case, the indicator element may be visible from externally of the package and be such as to be exposed to air (so that the observable change occurs) upon opening or disturbance (eg. by a syringe) of the package. Thus, if there has been unauthorised prior opening of the package then this will be immediately evident upon inspection of the package.

In the case of protection against counterfeit goods, the indicator element (sealed against exposure to air) may be provided anywhere in or on the package. The element may, for example, be part of a removable wrapping around a box or the like in which the product is sold such that removal of the wrapping causes exposure of the element to air. The indicator element may incorporate a written message and/or pattern which appears upon exposure to the air. Thus, a purchaser of the product is able, by breaking the seal between the indicator element and the air, to reveal the message or pattern which is characteristic of the "genuine article" and thus confirm that he/she has not purchased a counterfeit product. Whilst in theory the same type of indicator element could also be incorporated in or on the packaging of a counterfeit product, it does provide a further hindrance to the supplier of counterfeit goods.

The indicator element which produces an observable change on exposure to air preferably incorporates a formulation which produces a colour change as a result of solvent evaporation on exposure to air. As a general principle, such formulations preferably incorporate a colourless dye precursor dissolved in a volatile organic solvent and an acidic medium which (when the solvent evaporates) causes the dye precursor to become strongly coloured.

Examples of such colourless dye precursors are colour formers, such as the lactone forms of cationic dyes, the carbinol bases of cationic dyes and leuco forms of cationic dyes (preferably triphenyl methanes and xanthenes). The preferred class are the lactone derivatives which provide a whole spectrum of colours from yellow, through red and blue, to green and black.

A typical example of a lactone colour former of the xanthene type is given in structure (1).



in which R, R<sub>1</sub> and R<sub>2</sub> are the same or different and may be hydrogen, alkyl (e.g. C<sub>1-5</sub> alkyl), optionally substituted aryl, cycloalkyl (e.g. cyclohexyl), and alkenyl.

For preference R<sub>2</sub> is an alkyl group (most preferably a methyl group).

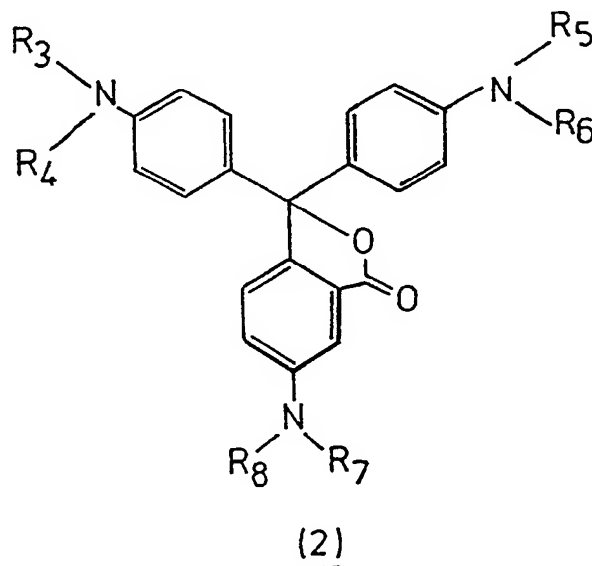
Examples of compounds of formula (1) suitable for use in the invention include those in which

R = R<sub>1</sub> = -C<sub>2</sub>H<sub>5</sub>; R<sub>2</sub> = -CH<sub>3</sub>

R = -CH<sub>3</sub>; R<sub>1</sub> = cyclohexyl; R<sub>2</sub> = -CH<sub>3</sub>

R = -C<sub>2</sub>H<sub>5</sub>; R<sub>1</sub> = p-methylphenyl; R<sub>2</sub> = -CH<sub>3</sub>

A representative lactone derivative of a triphenyl methane dye is given by formula (2).



in which  $R_3-R_8$  are the same or different and are as defined for  $R$ ,  $R_1$  and  $R_2$ .

For preference  $R_3-R_8$  are  $C_{1-5}$  alkyl groups. Preferably  $R_3-R_8$  are identical and are most preferably methyl groups. The compound of formula (2) in which  $R_3-R_8$  are all methyl groups is Crystal violet lactone and is a preferred compound for use in the invention. Crystal violet lactone changes from colourless to blue in the presence of an acidic medium.

Examples of suitable volatile organic solvents include ketones (eg. acetone, butanone), alcohols (eg. ethanol, methanol) and esters (eg. ethyl acetate).

Dye precursor concentration is preferably 0.1 to 10 per cent, more preferably 0.1 to 1.0 per cent.

One composition which we have found to be particularly suitable comprises Crystal Violet Lactone formulated in a suitable solvent for application to a substrate which is or incorporates an acidic material which promotes the colour formation reaction. The substrate may for example be Thin Layer Chromatography paper which provides silicic acid as the aforementioned acidic material. Other substrates (eg. paper, metal etc.) when coated with an acidic substance (eg. phenols, such as Bis Phenol A; acids; clays) would also give the effect.

The invention will be further described by way of example only with reference to the accompanying drawings, in which

Fig. 1 illustrates one embodiment of package in the form of a container in accordance with the invention prior to initial opening of the container;

Fig. 2 illustrates removal of the closure member from the container;

Fig. 3 is a plan view of the cap of the container after opening thereof;

Fig. 4 is a modification of Fig. 1;

Fig. 5 is a schematic view of a further embodiment of package in accordance with the invention;

Fig. 6 is a schematic view of a sealing tape; and

Figs. 7a, 7b and 8 illustrate applications of the tape illustrated in Fig. 6.

The container 1 illustrated in Fig. 1 comprises a jar, bottle or the like 2 (hereinafter referred to simply as a bottle) having a screw-threaded neck 3 on which locates a closure cap 4. The mounting of this cap 4 on the neck 3 is such that removal of the cap 4 (from the bottle 2) is effected by pushing the cap 4 downwardly towards the body of the bottle 2 and then unscrewing the cap 4. This type of arrangement is already used, for example, on bottles or jars of medicines (eg. pills).

Within the top of the closure cap 4 is a layer of TLC paper 5 located between the inner upper surface of the cap 4 and an air tight barrier membrane 6. With the cap 4 in position, the membrane 6 is located just above the lip of the bottle 2.

The TLC paper is treated over a circular area thereof (see below) with a formulation (eg. of the type described above) which changes colour on solvent evaporation caused by exposure to the air. The TLC paper is visible through a transparent area 7 in the top of the cap (see Fig. 3).

A removable induced seal cap 8 is provided in the neck of the bottle 2 as shown.

Prior to assembly into the form illustrated in Fig. 1, the container 1 will be provided with its contents which may be, for example, a food product or a medicine. The container 1 as illustrated in Fig. 1 is thus in the form in which it will be distributed (eg. to supermarkets) containing the desired product.

To open the container 1, the cap 4 is pushed downwardly (as explained above) prior to unscrewing of the cap. The downward push of the cap 4 causes the rim of the bottle 2 to break the membrane 6 so that the TLC paper 5 is exposed to air (see Fig. 2). As a result, the formulation with which the TLC paper is marked is caused to



change colour, which colour change becomes visible as an area 9 (assumed to be circular) over which the TLC paper was treated with the formulation. The colour change is visible through this transparent area 7 of the cap 4.

It will thus be appreciated that the fact that the cap 4 has been removed is immediately evident by virtue of the colour change visible through the transparent area 7. It is thus an easy matter to tell whether there has been any unauthorised opening of the container 1 (prior to its purchase) such as may indicate that the contents of the container have been tampered with.

Although the air sensitive ink has been shown as having been applied over a circular area 9, the ink could equally well have been applied in the form of a written message warning that the container had previously been opened.

Once the container 1 has been opened, access to the contents may be gained by removing the replaceable induced seal cap 8.

Fig. 4 is a modification of the container shown in Fig. 1. For convenience, like parts in Figs. 1 and 4 are identified by the same reference numeral but suffixed (in Fig. 4) by the letter "a". The modification of Fig. 4 consists in that the rim is a raised point 10 which, when the top 4a is unscrewed for the first time, causes rupture of the membrane 6a.

Referring now to Fig. 5 there is illustrated container lid 21 with an indented section 22 which "pops up" when the lid 21 is first removed. Such containers are already used for the packaging of baby foods.

In the arrangement shown in Fig. 5, the indented section 22 is provided with a small projection 23 which, when the indentation 22 "pops up", is adapted to puncture an air-tight barrier membrane 24. Additionally, an air sensitive indicator element 25 (eg. comprising Crystal Violet Lactone dissolved in a solvent on an acidic substrate), is provided on the surface of the indentation 22. Upon initial opening of the container 22, the lid 21 is unscrewed, causing the projection 23 to rise thus puncturing the membrane 24 and exposing the indicator element 25 to the air so that an observable change takes place.

Fig. 6 shows a tape 30 which may be used for providing seal on a package. The illustrated tape 30 comprises a clear film 31 which

overlies a layer 32 comprised of TLC paper 31 treated with a formulation as described above. As shown in Fig. 6, the TLC paper is visible through the film 31, which film 31 is provided (on the side of the TLC paper) with an adhesive coating. This adhesive coating is only provided on that portion of the area of film 31 which does not overlie the TLC paper 32.

Figs. 7a and 7b show two ways in which the tape 30 may be applied around the lid of a container. In both cases, the adhesive attachment of the film 31 to the jar and lid seals the TLC paper against exposure to air. Upon removal of the lid, this seal is broken so that the TLC paper is exposed to air, solvent evaporates and the colour change occurs.

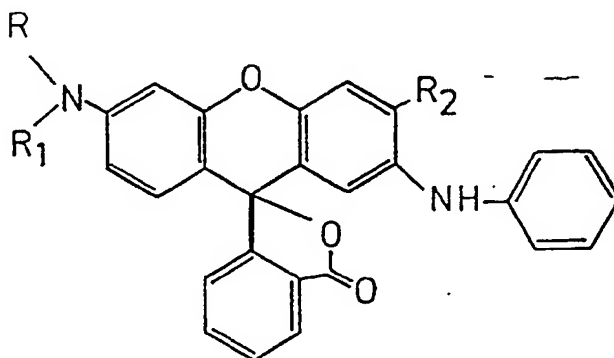
The strip 30 illustrated in Fig. 6 may also be provided as a "tear-off" strip around a package, as illustrated in Fig. 8. Removal of the tear-off strip causes the ink to be exposed to air with the consequential colour change.

In a modification of the strip illustrated in Fig. 6, the TLC layer may be provided with apertures. Thus, upon removal of the strip 30, air may pass through these apertures from the reverse side of the TLC paper so as to effect the colour change of the ink in addition to air which passes the edging of the TLC layer between the adjacent surfaces of this layer and the layer 31.

CLAIMS

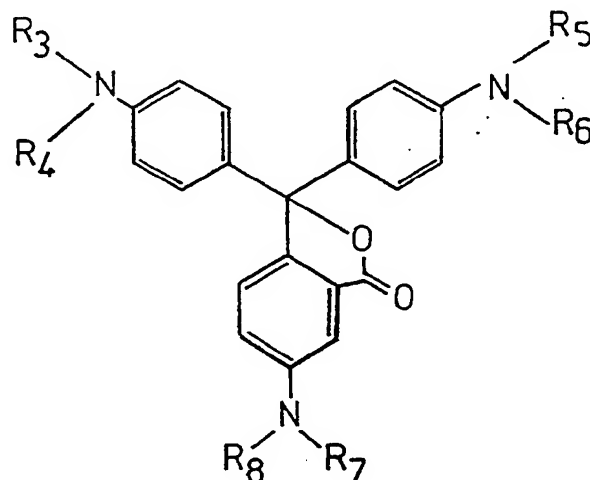
1. Packaging associated with an air sensitive indicator element which is prevented from contact with air, said indicator element being such as to provide an observable change upon exposure to air.
2. Packaging as claimed in claim 1, wherein the indicator element is visible from externally of the package and is such as to be exposed to air upon opening or disturbance of the package.
3. Packaging as claimed in claim 1 or claim 2, wherein the indicator element is provided on a removable lid of a container and a barrier layer is provided to protect the indicator element from exposure to air, the barrier layer being broken or punctured upon removal of the lid from the container.
4. Packaging as claimed in claim 3, wherein the barrier layer is broken by a rim of the container during removal of the lid from the container.
5. Packaging as claimed in claim 3, wherein a portion of the lid is adapted to move relative to the remainder of the lid when the lid is removed from the container, said portion being provided with means to break the barrier layer upon removal of the lid from the container.
6. Packaging as claimed in claim 1, wherein the indicator element is provided on a strip attached to the package, the strip being broken upon opening the package or removed prior to opening the package.
7. Packaging as claimed in claim 1, wherein the indicator element is part of a removable wrapping around a box or the like in which the product is sold such that removal of the wrapping causes exposure of the element to air.
8. Packaging as claimed in any preceding claim, wherein the indicator element incorporates a written message which appears upon exposure to air.
9. Packaging as claimed in any preceding claim, wherein the indicator element incorporates a formulation which produces a colour change as a result of solvent evaporation on exposure to air.
10. Packaging as claimed in claim 9, wherein the formulation which produces the colour change incorporates a colourless dye precursor dissolved in a volatile solvent, and an acidic medium which on evaporation of the solvent causes the dye precursor to become coloured.

11. Packaging as claimed in claim 10, wherein the dye precursor comprises a lactone form of a cationic dye.
12. Packaging as claimed in claim 10, wherein the dye precursor comprises a carbinol base of a cationic dye.
13. Packaging as claimed in claim 10, wherein the dye precursor comprises a leuco form of a cationic dye.
14. Packaging as claimed in any one of claims 11 to 13, wherein the cationic dye is a triphenyl methane dye.
15. Packaging as claimed in any one of claims 11 to 13, wherein the cationic dye is a xanthene dye.
16. Packaging as claimed in claim 11, wherein the dye precursor has the structure



in which R, R<sub>1</sub> and R<sub>2</sub> are the same or different and may be hydrogen, alkyl (e.g. C<sub>1-5</sub> alkyl), optionally substituted aryl, cycloalkyl (e.g. cyclohexyl), and alkenyl.

17. Packaging as claimed in claim 11, wherein the dye precursor has the structure



in which  $R_3$ - $R_8$  are the same or different and are as defined for  $R$ ,  $R_1$  and  $R_2$ .

18. Packaging as claimed in any one of claims 10 to 17, wherein the volatile solvent is a ketone.

19. Packaging as claimed in claim 18, wherein the ketone is acetone or butanone.

20. Packaging as claimed in any one of claims 10 to 17, wherein the volatile solvent is an alcohol.

21. Packaging as claimed in claim 20, wherein the alcohol is ethanol or methanol.

22. Packaging as claimed in any one of claims 10 to 17, wherein the volatile solvent is an ester.

23. Packaging as claimed in claim 22, wherein the ester is ethyl acetate.

24. Packaging as claimed in any one of claims 10 to 23, wherein the dye precursor concentration is 0.1 to 10 per cent.

25. Packaging as claimed in claim 24, wherein the dye precursor concentration is 0.1 to 1.0 per cent.

26. Packaging as claimed in claim any one of claims 10 to 25, wherein the acidic medium is or is incorporated into a substrate on which the dye precursor is provided.

27. Packaging as claimed in claim 26, wherein the substrate is Thin

Layer Chromatography paper.

28. Packaging as claimed in any one of claims 10 to 27, wherein the acidic medium is silicic acid.

29. Packaging as claimed in any one of claims 10 to 27, wherein the acidic medium is a phenol.

30. Packaging as claimed in claim 29, wherein the phenol is Bis Phenol A.

31. Packaging as claimed in any one of claims 10 to 27, wherein the acidic medium is a clay.

32. An air sensitive indicator element for use in packaging, wherein said indicator element incorporates a formulation which produces a colour change as a result of solvent evaporation on exposure to air.

33. Indicator element as claimed in claim 32, wherein the formulation which produces the colour change incorporates a colourless dye precursor dissolved in a volatile solvent, and an acidic medium which on evaporation of the solvent causes the dye precursor to become coloured.

34. Packaging as claimed in claim 16 wherein  $R_2$  is an alkyl group, most preferably a methyl group.

35. Packaging as claimed in claim 16 wherein

$R = R_1 = -C_2H_5$ ;  $R_2 = -CH_3$ ; or

$R = -CH_3$ ;  $R_1 = \text{cyclohexyl}$ ;  $R_2 = -CH_3$ ; or

$R = -C_2H_5$ ;  $R_1 = \text{p-methylphenyl}$ ;  $R_2 = -CH_3$ .

36. Packaging as claimed in claim 17 wherein the dye precursor is Crystal violet lactone.

37. Packaging substantially as hereinbefore described, with reference to Figures 1 to 4 of the accompanying drawings.

38. Packaging substantially as hereinbefore described, with reference to Figure 5 of the accompanying drawings.

39. Packaging substantially as hereinbefore described, with reference to Figures 6 to 8 of the accompanying drawings.

**Patents Act 1977**  
**Examiner's report to the Comptroller under**  
**Section 17 (The Search Report)**

-12-

Application number

9200272.4

**Relevant Technical fields**

- (i) UK CI (Edition K ) B8C (CWS4, CWS8) ; B8F (FBG) ;  
B8T (TTB, TTC, TTT)
- (ii) Int CI (Edition 5 ) B65D 55/02, 55/06 ;  
G09F 3/02, 3/03

**Search Examiner**

ALEX LITTLEJOHN

**Databases (see over)**

(i) UK Patent Office

**Date of Search**

(ii)

20 MARCH 1992

**Documents considered relevant following a search in respect of claims**

1-39

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
Y	EP 0257468 A2 (GENERAL ELECTRIC) see eg Figures 2 and 4	5
X	WO 90/03632 A1 (RICHARDSON) see eg Figures 2-4 and page 7 lines 21-28 and note GB equivalent 2242817	1,2, 6-36
X	US 4945708 (CURIEL) see eg column 6 lines 16-32	1-3, 7-36
X	US 4813541 (VELASCO) see whole document	1,8-36
X,Y	US 4519515 (SCHONBERGER) see whole document	X:1-4, 8-36 Y:5
X,Y	US 4511052 (KLEIN) see whole document	X:1-4, 8-36 Y:5
X,Y	US 4505399 (WEINER) see whole document	X:1-4, 8-36 Y:5
X,Y	US 4502605 (WLOSZCZYNA) see whole document	X:1-4, 8-36 Y:5

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Category	Identity of document and relevant passages	Relevant to claim(s)

### Categories of documents

**X:** Document indicating lack of novelty or of inventive step.

**Y:** Document indicating lack of inventive step if combined with one or more other documents of the same category.

**A:** Document indicating technological background and/or state of the art.

**P:** Document published on or after the declared priority date but before the filing date of the present application.

**E:** Patent document published on or after, but with priority date earlier than, the filing date of the present application.

**&:** Member of the same patent family, corresponding document.

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